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(54) Water Treatment System

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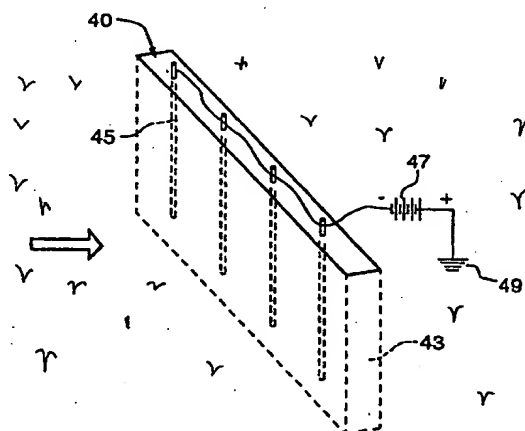
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(54) Title: WATER TREATMENT SYSTEM



(57) Abstract

Treatment of halogenated hydrocarbon contaminants in groundwater is accomplished by passing the water through a bed of granular iron (43). An electrical circuit (47) is promoted for providing electrons for reducing the contaminant. The circuit may be made using a DC supply, by configuring an electrolytic circuit, or by providing a layer of a second metal such as zinc placed next to the iron bed, thereby creating a galvanic circuit.

1 Title WATER TREATMENT SYSTEM

2

3 This invention relates to the treatment of water, especially
4 groundwater, contaminated with halogenated hydrocarbons, such
5 as carbon tetrachloride. Such contaminants can be difficult
6 to treat in groundwater, because their natural degradation
7 rate is very slow, they are transported long distances through
8 the aquifer with the groundwater, and they are hazardous even
9 in very small trace concentrations if they get into drinking
10 water supplies.

11

12 BACKGROUND TO THE INVENTION

13

14 Patent publication WO-91/08176 disclosed the technique of
15 passing water contaminated with an halogenated hydrocarbon
16 through a (permeable) body of a metal, for example through a
17 body of granular iron. The body of granular iron was placed
18 in a trench excavated in the ground in the path of an oncoming
19 plume of the contaminated groundwater, whereby the groundwater
20 was caused to pass through the metal. Or, the contaminated
21 water was taken out of the ground, and passed through a
22 container of granular iron.

23

24 Developments of that technology are disclosed in WO-92/19556
25 and in WO-92/19545.

26

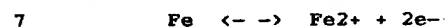
27 Provided there is a substantial residence time, and provided
28 that strictly reducing conditions can obtain over a prolonged
29 period, traces of halogenated hydrocarbons in the water can be
30 caused to break down chemically in the presence of the iron or

1 other metal.

2

3 It is surmised that the chemical breakdown reaction may be
4 explained as follows:

5 Under the conditions of the process, iron metal oxidizes to
6 the ferrous ion, releasing two electrons, i.e.



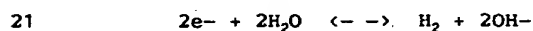
8 The halogenated hydrocarbon may be regarded as comprising a
9 carbon-halogen component, C-Hal, and a hydrogen ion. Upon
10 interacting with the electrons, the carbon reacts with the
11 hydrogen ion to form a relatively non-hazardous hydrocarbon,
12 such as methane gas, and halogen ion in solution, e.g. chloride
13 etc.



15 Thus, the halogenated hydrocarbon breaks down in the presence
16 of iron, under reducing conditions.

17

18 However, what can also happen is that electrons available from
19 the iron could, under reducing conditions, cause the
20 surrounding water to dissociate, i.e.



22 The H_2 bubbles off as hydrogen gas, but the presence of the
23 2OH^- serves to raise the pH of the water, which can rise high
24 enough, say to 9 or 10, that dissolved inorganic species
25 present in the water, which precipitate out of solution at
26 high pH, can start to do so. At high pH, for example,
27 carbonates of various kinds, which are nearly always present
28 in groundwater, can precipitate.

29

1 Under high pH conditions (i.e a pH of 9 or 10) the ferrous
2 ions, if plentiful, could combine with the dissolved
3 substances, and ferrous carbonate or ferrous hydroxide may
4 precipitate.

5
6 The precipitates are a problem for the process of
7 decomposition of halogenated hydrocarbons because they tend to
8 become deposited in the pore spaces of the body of granular
9 iron, and to clog up the body, making the body not so
10 permeable to the flow of groundwater.

11
12 The invention is aimed generally at promoting the breakdown of
13 the halogenated hydrocarbon. The invention is particularly
14 aimed at inhibiting the precipitation of the iron species and
15 other substances from solution, which, if permitted, might
16 reduce the permeability of the body of granular iron, and
17 might coat the particles of iron with substances that would
18 impede the reduction of the halogenated contaminant.

19

20

21 GENERAL FEATURES OF THE INVENTION

22

23 The invention lies in providing a body of a first metal, for
24 example iron, the metal being in finely divided powder,
25 particulate, or granular form, and the body being porous and
26 permeable enough for the water to pass therethrough.

27

28 Conditions should be maintained whereby oxygen and oxidising
29 agents are excluded from the body of metal and from the water.
30 One preferred manner in which oxygen may be excluded lies in

1 the fact that the process is carried out below the water
2 table.

3
4 It may be noted that if there is any oxygen present in the
5 water, that oxygen will have to be removed from the water
6 before the breakdown reaction will start. If only small
7 quantities of oxygen are present, that is not very important,
8 because the oxygen will usually be quickly used up in
9 oxidizing small quantities of the metal. When all the oxygen
10 that was dissolved in, or was otherwise available in, the
11 water has been used up, the breakdown reaction may be expected
12 to commence. Large quantities of dissolved oxygen would be a
13 problem in the invention, however, because then much of the
14 metal would simply be wasted through being oxidised, and
15 because the reducing conditions required for the breakdown
16 reaction would not be obtainable.

17
18 The invention lies in setting up an electrochemical circuit,
19 by making the first metal an electrode, and maintaining the
20 first metal at a potential relative to the surrounding water.

21

22

23 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

24

25 By way of further explanation of the invention, exemplary
26 embodiments of the invention will now be described with
27 reference to the accompanying drawings, in which:

28

29 Fig 1 is a diagrammatic view of a system for treating
30 contaminated water in a canister or tank;

1 Fig 2 is a diagrammatic view of a system for treating
2 contaminated groundwater in-situ;
3 Fig 3 is a diagrammatic view of another system for treating
4 contaminated groundwater in-situ;
5 Fig 4 is a diagrammatic view of a further system for treating
6 contaminated groundwater in-situ.

7
8 The apparatuses shown in the accompanying drawings and
9 described below are examples which embody the invention. It
10 should be noted that the scope of the invention is defined by
11 the accompanying claims, and not necessarily by specific
12 features of exemplary embodiments.

13
14 In Fig 1, a tank or container 20 is provided, which in this
15 case is made of an electrically-non-conducting material, being
16 a plastic material.

17
18 Into the tank 20 is placed a body 23 of treatment material,
19 which comprises a body of granular iron. The body of granular
20 iron is so constituted that the body is porous or permeable to
21 the passage of water therethrough.

22
23 The tank 20 is provided with inlet 25 and outlet 27 pipes, for
24 conducting water through the tank. The body of granular iron
25 completely fills the cross-sectional shape of the tank,
26 whereby water cannot pass through the tank from the inlet to
27 the outlet other than by passing through the granular iron.

28
29 Electrodes 29,30 are placed at the ends of the tank, close to
30 the inlet and the outlet respectively. The electrodes should

1 be of stainless steel or other non-corrosive conductor. The
2 electrodes are coupled to a DC battery 32, whereby a voltage
3 and current are applied between the two electrodes.

4
5 The body 23 of granular iron is so set up in the tank 20 that
6 the electrodes 29,30 are in electrical contact with the
7 opposite ends of the body of granular iron, whereby the
8 voltage and current are applied to the body.

9
10 In use, water contaminated with an halogenated hydrocarbon is
11 fed through the tank 20. The presence of the voltage and
12 current has been observed to increase the rate at which the
13 halogenated hydrocarbon breaks down; and also has been found
14 to inhibit the deposition of iron and other precipitates.

15
16 In a particular example, a column 10 cm in length and 8 cm in
17 diameter was packed with granular iron having a mean grain
18 diameter of 100 mesh. Water containing 10 milligrams per
19 litre of tetrachloroethene (PCE) in solution was passed
20 through the column. About 2 volts DC was applied across the
21 stainless steel electrodes, resulting in a flow of electrons
22 through the column.

23
24 It was observed that the rate of degradation of the PCE (ie
25 the concentration of PCE in the outlet compared with the
26 concentration of PCE in the inlet) speeded up by a factor of
27 about three times. From this, it may be surmised that the
28 electric current acts as an additional source of electrons
29 (additional, that is, to the electrons arising from the
30 oxidation of the iron), resulting in increased rates of

1 removal of the contaminants.

2

3 Fig 2 shows an arrangement suitable for in-situ (i.e in-
4 ground) operation, for treating contaminated groundwater while
5 the water remains in the ground.

6

7 Here, a trench 40 is excavated in the material of the aquifer,
8 and the body 43 of granular iron is placed in the trench. The
9 body 43 may comprise granular iron mixed with sand, as an
10 inert filler, for bulk, (so long as adequate electrical
11 conductivity was maintained in the body), or granular iron
12 mixed with an adsorbing agent, such as activated carbon. As
13 mentioned in WO-92/19556, the adsorbent retards the dissolved
14 contaminants while the water passes through un-retarded,
15 whereby the contaminants are retained in the trench (and close
16 to the granular iron) for a much longer period of time than
17 the water itself stays in the trench. Providing the adsorbent
18 maximises the likelihood that there is time for the breakdown
19 reaction to be completed, while minimising the needed quantity
20 of granular iron.

21

22 In Fig 2, electrodes, comprising rods 45 of stainless steel,
23 are inserted in the body 43 of granular iron. The electrodes
24 are coupled to a DC battery 47, and the other side of the
25 battery is grounded, as at 49. Thus, the electrical circuit
26 is completed through the material of the aquifer and through
27 the groundwater.

28

29 It might be considered from the diagrams that in Figs 1 and 2
30 the whole body of granular iron constitutes the one electrode.

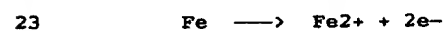
1 The iron itself, of course, being a metal, and conductive,
2 will not support very much of a voltage gradient.

3
4 It might be surmised that, insofar as the body 43 of iron is
5 itself an electrode, that the body of iron should be the
6 anode, whereby the oxidation of the iron would be enhanced,
7 releasing more electrons.

8
9 However, it is observed that the breakdown of the halogenated
10 hydrocarbon is enhanced when the iron is made the cathode, and
11 it is observed that the breakdown proceeds at a faster rate.
12 Also, it is observed, when the iron is made the cathode, that
13 there is less deposition of precipitated material present in
14 the iron bed.

15
16 It may be surmised that, in order for the halogen breakdown to
17 be speeded up, the conditions must have been favouring
18 reduction of the halogen in the iron bed, at the expense of
19 oxidation of the iron, while oxygen evolution was happening at
20 the anode.

21
22 In the iron bed, the iron oxidation reaction is:



24 This is the reaction that is slowed by the fact that the iron
25 bed is the cathode.

26
27 At the anode, the oxygen evolution reaction, due to the
28 electrolysis of the water, proceeds as



1 whereby the H^+ , upon entering solution, also results in a
2 lowering of the pH.

3

4 Making the iron bed the cathode results in the favouring of
5 reduction of the halogen contaminant at the expense of iron
6 oxidation, while oxygen evolves at the anode. The pH is
7 lowered, at least near the anode, and precipitation of iron
8 compounds is lowered because of the lower iron oxidation.

9

10 In order for the reduction of the halogenated hydrocarbon to
11 proceed, the conditions must remain reducing, and the system
12 designer should ensure that reducing conditions are favoured.
13 This may be done, in an in-ground treatment system, for
14 instance, by providing that all the iron is placed well below
15 the water table. Also, for instance, the oxygen gas that
16 bubbles off the anode due to electrolysis of the water must
17 not be allowed to come in contact with or pass through the
18 iron bed. In a treatment installation, the system designer
19 should see to it that the anode is so located that oxygen
20 bubbling therefrom will not pass through the bed of iron.

21

22 The anode may be configured as a separate series of stainless
23 steel rods inserted in the aquifer material, downstream of the
24 iron bed. Any oxygen bubbling off the anode then would not
25 affect the iron bed.

26

27 In considering why the halogen reduction proceeds quicker when
28 the iron bed is made the cathode, it may be noted that in fact
29 the number of electrons produced by the naturally-oxidizing
30 iron is already ample. Therefore, the body of iron may be

1 made the cathode. Although this inhibits oxidation of the
2 iron, the benefit of making the iron the cathode is that less
3 of the iron precipitates.

4
5 It should be pointed out that the reduction of the halogenated
6 hydrocarbon, by the use of electricity, requires that the
7 electrode (preferably the cathode) at which the reduction
8 takes place is of a large surface area. The granular iron
9 provides such a large-area electrode.

10
11 Fig 3 shows an in-ground water treatment installation, in
12 which a trench 50 is excavated in the path of an on-coming
13 plume 52 of a groundwater contaminant, being a halogenated
14 hydrocarbon such as carbon tetrachloride. In the trench 50 is
15 placed a body 54 of granular iron.

16
17 Located on top of the body 54 of granular iron is a layer 56
18 of zinc filings. In place of zinc, another metal may be used
19 having a lower potential than iron. The zinc filings are
20 placed directly on top of the granular iron, whereby
21 electrical contact is made between the two metals.

22
23 The zinc is placed below the water table 58, and the space 60
24 above the water table is filled in with sand, or other
25 available filler material.

26
27 No outside source of electricity is connected to the metals,
28 but in fact the metals themselves in this configuration serve
29 to generate an electric current. In an iron/zinc pair, the
30 iron becomes the cathode and the zinc the anode.

1
2 The zinc oxidizes, $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$, which creates the
3 supply of electrons needed for the breakdown of the
4 contaminant. The iron is not called upon to oxidize, and to
5 supply electrons for the reduction of the contaminant. There
6 may be some deposition of precipitates, such as zinc
7 carbonate, in the zinc layer, but that does not matter so
8 much, especially if the treatment system is arranged so that
9 the water, or most of the water, is not actually required to
10 pass through the zinc layer. The main bulk of material on
11 which the breakdown of the contaminant occurs remains the
12 iron. Iron is considerably cheaper than zinc in bulk
13 quantities, and besides, iron is relatively harmless if it
14 should become dissolved in the groundwater -- if forced to
15 choose, most authorities would prefer to have Fe^{2+} in the
16 treated groundwater rather than Zn^{2+} .

17
18 It may be noted that mixing or dispersing the zinc in with the
19 iron has less effect in promoting the breakdown of the
20 halogenated hydrocarbon. The zinc should preferably be placed
21 in a layer, as described, whereby the layer of zinc can act as
22 a separate electrode with respect to the bed of iron.
23 However, it is also contemplated that the zinc may be placed
24 in two or more layers disposed through the iron.

25
26 The zinc may be placed on top of the bed of iron, as shown;
27 or, the zinc may be placed in series with the bed of iron in
28 the ground. Patent publication WO-93/22241 shows a funnel-
29 and-gates treatment system; in that system, contaminated water
30 is funnelled through a gate, in which is placed the treatment

1 material. In Fig 4, a barrier 60 is placed in the ground, and
2 the moving groundwater is funnelled into a gate 63. In the
3 gate is placed a bed of granular iron 65. Behind the bed of
4 iron (i.e in the gate, but downstream of the iron) is placed a
5 bed of zinc 67. The zinc and the iron are arranged so as to
6 promote the electrochemical activity as described. The zinc
7 should be so placed in relation to the iron that the electrons
8 arising from the oxidation of the zinc are donated to the
9 iron.

10

11 The zinc, being a metal of lower potential than the iron, and
12 arranged as an anode, donates electrons by galvanic action.
13 Applying supplied electricity to the first metal as one
14 electrode, the other electrode being separated, the electrons
15 are provided by electrolytic action. As described, both the
16 galvanic and the electrolytic actions may be utilized to
17 enhance the breakdown of halogenated hydrocarbons in
18 groundwater.

19

20 Although the invention has been described as it relates to
21 treatment using iron, other metals may be used, for example:
22 zinc, aluminum, magnesium, other transition metals, and metal
23 couples such as copper coated iron.

24

25 The invention may be used to treat a wide range of organic
26 contaminants, including aliphatics, aromatics, and
27 polyaromatics with halogen and nitrogen group substituents
28 (although the invention has been described as it relates to
29 the treatment of halogenated hydrocarbons). Examples include
30 solvents such as carbon tetrachloride, tetrachlorethene, and

- 1 hexachlorethane; hexachlorobenzene, nitrosamines, explosives
- 2 such as trinitrotoluene, PCP's, nitro-PAH's, and certain
- 3 pesticides.
- 4

Claims

- 1
2 CLAIM 1. Procedure for treating water contaminated with an
3 organic contaminant, comprising the steps of;
4 providing a body of a first metal, the metal being in finely
5 divided particulate form, and the body being porous and
6 permeable enough for the water to pass therethrough;
7 passing the contaminated water therethrough;
8 creating and maintaining reducing conditions in the body of
9 the first metal and in the water passing therethrough;
10 providing an electrochemical circuit, by making the first
11 metal an electrode, and maintaining the first metal at a
12 potential relative to the surrounding water.
13
- 14 CLAIM 2. Procedure of claim 1, wherein the contaminant is a
15 halogenated hydrocarbon.
16
- 17 CLAIM 3. Procedure of claim 1, wherein the first metal is
18 iron.
19
- 20 CLAIM 4. Procedure of claim 1, including the step of so
21 configuring the electrochemical circuit that the body of the
22 first metal is a cathode in the circuit.
23
- 24 CLAIM 5. Procedure of claim 1, including the steps of:
25 placing the body of the first metal in an aquifer, or in the
26 - ground;
27 wherein the contaminated water is groundwater, in the aquifer;
28 and so arranging the body of the first metal in the aquifer
29 that the contaminated groundwater passes therethrough.
30

1 CLAIM 6. Procedure of claim 5, including the step of locating
2 the body of the first metal substantially wholly below the
3 water table.
4

5 CLAIM 7. Procedure of claim 5, including the steps of:
6 creating an electrolytic circuit, comprising two electrodes,
7 being an anode and a cathode, and an electrolyte;
8 configuring the body of the first metal as one electrode, and
9 surrounding aquifer or ground material as the second
10 electrode, and the groundwater as the electrolyte;
11 and applying a voltage between the two electrodes.
12

13 CLAIM 8. Procedure of claim 7, including the step of applying
14 the voltage to the body of the first metal through a
15 conductor, which comprises a metal rod or rods inserted into
16 the body.
17

18 CLAIM 9. Procedure of claim 7, including the step of applying
19 the voltage such that the body of the first metal is the
20 cathode of the electrolytic circuit.
21

22 CLAIM 10. Procedure of claim 5, including the steps of:
23 creating a galvanic circuit, comprising two electrodes, being
24 an anode and a cathode, in electrical contact with each
25 other;
26 providing a body of a second metal, and placing the body of
27 the second metal in electrical contact with the body of the
28 first metal;
29 so configuring the galvanic circuit that one of the bodies of
30 metal is the anode, and the other body of metal is the

1 cathode, of the galvanic circuit.

2

3 CLAIM 11. Procedure of claim 10, including the step of
4 providing the second metal in the form of a metal that is
5 more electro-positive than the first metal, whereby the
6 second metal becomes the anode, and the first metal the
7 cathode, of the galvanic circuit.

8

9 CLAIM 12. Procedure of claim 11, wherein the second metal is
10 zinc.

11

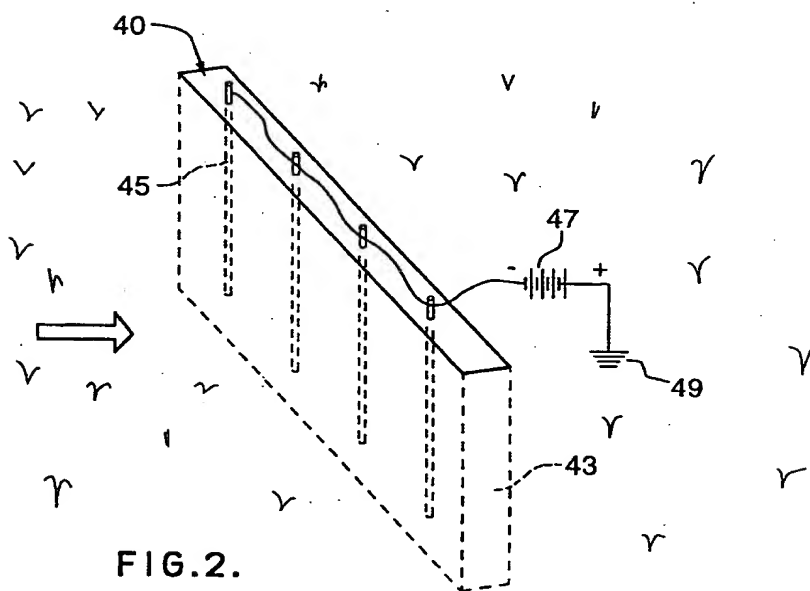
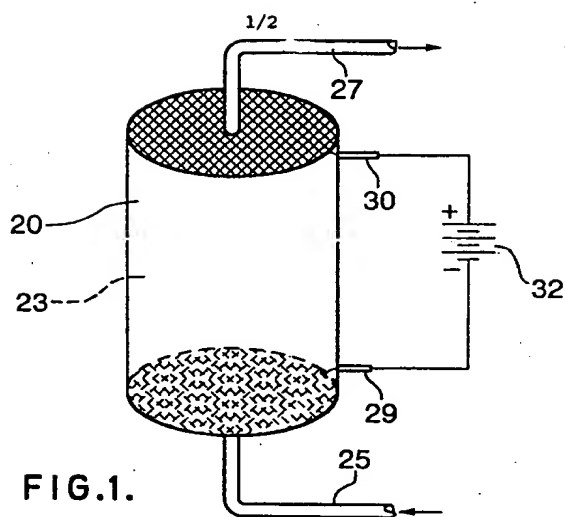
12 CLAIM 13. Procedure of claim 11, including the step of
13 arranging the two bodies as separate structures or layers,
14 which are arranged for electrical contact with each other,
15 but are so arranged that the two metals are substantially
16 not mixed together.

17

18 CLAIM 14. Procedure of claim 13, including the step of
19 physically arranging the bodies so that a majority of the
20 contaminated groundwater passes through the first metal, but
21 does not pass through the second metal.

22

23 CLAIM 15. Procedure of claim 12, including the step of:
24 placing the body of the first metal in a trench, the trench
25 being located in the path of an oncoming plume of the
26 contaminated groundwater;
27 placing the body of the second metal in the trench, and on top
28 of the body of the first metal;
29 and so arranging the trench and the bodies therein that the
30 body of the second metal lies below the water table.



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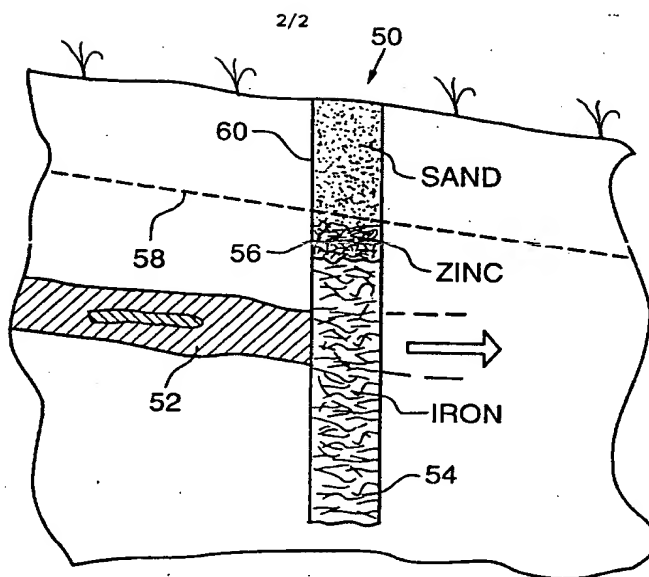


FIG. 3

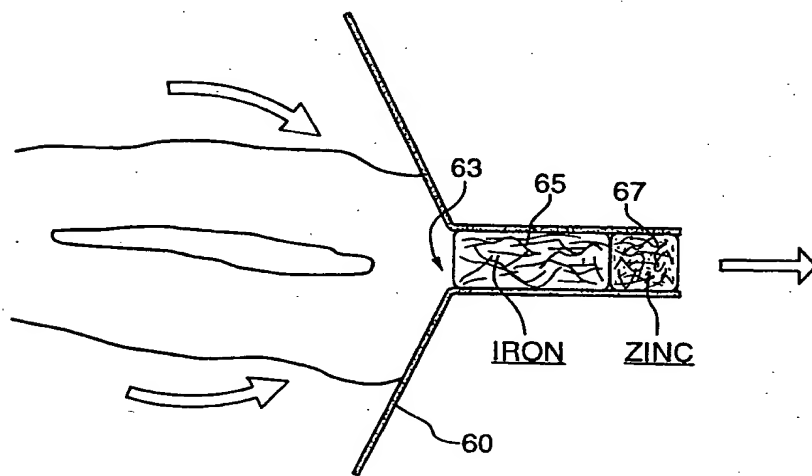


FIG. 4

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